



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in or relating to Pigments

We, E.I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved hydrous iron oxide pigment compositions and their production and to coating compositions containing the same. More particularly, the invention relates to a method of improving hydrophobic iron oxide pigment product having a particle-size below the visible light-scattering level and to organic coating compositions and finishes containing this pigment which exhibit superior transparency, brilliance, two-tone effect and depth of mass tone in comparison with coating compositions and finishes containing ordinary hydrous iron oxide pigment transferred to the organic film-forming compositions by methods well known to the art.

The value of iron oxide pigments in coating compositions is well established but although they provide durable coatings, the coatings pigmented with ordinary iron oxide do not have significant aesthetic appeal. Common iron oxide pigments ordinarily have a particle-size diameter in the range of about 250 to about 600 millimicrons. Because this particle-size is significantly above the visible light-scattering level, compositions pigmented with these ordinary iron oxide pigments are opaque and have good hiding power.

Specification No. 630,334 teaches a method of preparing hydrous iron oxide pigments having an average particle-size diameter of less than 100 millimicrons, ordinarily less than 50 millimicrons, and a method of transferring water-wet pulp of such hydrous iron oxide pigment to lacquer coating compositions to provide durable finishes which are substantially transparent. Such pigment provided a basis for formulating glamorous metallic finishes for automobiles of which "Duco" Lacquer Metalli - Chrome Enamels are representative. ("Duco" is a Registered Trade Mark). However, the particle-size distribution of this pigment includes a significant proportion of particles larger than the average particle size and ranging up to 300 millimicrons which are in the visible light scattering range causing the pigmented coatings prepared therefrom to vary in brilliance and transparency and to occasionally exhibit an undesirable milky or muddy appearance.

An important object of this invention is to provide an improved hydrous iron oxide pigment product which is free of pigment particles of diameter such that they scatter visible light, and which is readily dispersible in a hydrophobic organic film-forming material by mixing without expenditure of an excessive amount of mechanical energy.

The invention comprises hydrophobic iron oxide pigment compositions which comprise dispersions in a water-immiscible volatile organic liquid diluent of pigment particles having a molecularly thin surface coating of at least one hydrophobic aliphatic monocarboxylic acid which is soluble in the organic solvent, the said acid being bound by salt linkages to the pigment particles, and the said

dispersion being substantially free from pigment articles capable of scattering visible light. (The term "hydrophobic acid" is employed herein to denote an aliphatic monocarboxylic acid in which the radical joined to the carboxyl group is a hydrocarbon radical containing at least 5 carbon atoms).

Such compositions can be made, according to a further feature of the invention, from a water-wet hydrous iron oxide pigment pulp which has an average particle size (i.e. diameter) less than 100 millimicrons and a particle size distribution ranging from 1 to 300 millimicrons by (a) treating the wet pigment pulp with a solution of at least one hydrophobic aliphatic monocarboxylic acid in a non-reactive volatile water-immiscible organic liquid diluent in the proportion of 0.2-1.2 parts by weight of acid for each part by weight of iron oxide whereby the pigment particles are provided with a molecularly thin hydrophobic surface formed by the bonding of the said acid by salt linkages to the surface of the pigment particles, (b) removing free water from the resulting composition, and (c) fractionating the resulting composition centrifugally, if desired after adjusting its concentration, using a centrifugal force of at least 6000 g., to separate from the composition a pigment sludge fraction containing substantially all the pigment particles whose particle size is such that they scatter visible light. (The average particle size is as calculated on a weight basis).

The hydrous iron oxide pigment starting material may advantageously be a water-wet pigment pulp of hydrous ferric oxide or ferrous/ferric oxide, the preparation of which is described in Specifications Nos. 630,334 and 622,978. These pigment starting materials have an average particle size less than 100 millimicrons, ordinarily less than 50 millimicrons, and generally in the range of about 10-30 millimicrons, these averages representing particles ordinarily ranging from 1 to about 200 millimicrons with some particles as large as 300 millimicrons. The content of bound water of these hydrous iron oxide pigments ordinarily corresponds to about 15% based on the dry weight of the pigment pulp.

While the invention will now be described in more detail with particular reference to hydrous ferric oxide pigment compositions, the techniques described are equally applicable to pigment pulps derived by co-precipitation of ferric oxide with hydrous oxides of ferrous iron, chromium, aluminium, manganese and nickel, and the treatment of such pulps is within the scope of the invention. Similarly the resulting mixed oxide pigments are included in the term "iron oxide pigment" as used in this Specification.

In the general procedure of preparing hydrous ferric oxide pigment, an aqueous solution of a soluble ferrous salt, such as ferrous sulphate, is oxidised to the ferric salt, and the

pigment is struck from the solution by addition of a soluble hydroxide, such as caustic soda, to precipitate the hydrous ferric oxide, which is then washed substantially free from water-extractable salts.

In the practice of this invention, the resulting hydrous ferric oxide pulp of known ferric oxide content is added to a solution of a hydrophobic aliphatic monocarboxylic acid in a water-immiscible volatile organic solvent for the acid, and the mixture is agitated. In this treatment a substantial portion of the acid is bound to the surface of the pigment particles by salt linkages, thereby providing the pigment particles with a hydrophobic surface and causing liberation of water.

Lauric acid and coconut oil fatty acids are particularly preferred as the hydrophobic monocarboxylic acid reactant. More generally individual aliphatic monocarboxylic acids, saturated or ethylenically unsaturated having from 6 to 24 carbon atoms per molecule and mixtures thereof are usable, and can be substituted for the particular acids specified in the Examples given below, the substitution preferably being made on a molecular equivalent basis. Saturated aliphatic acids having from 8 to 16 carbon atoms per molecule are preferred. Fatty acids useful individually or in admixture include, besides lauric acid and the coconut oil fatty acids already referred to, capric, caprylic, caproic, myristic, palmitic, stearic, carnaubic, behenic, margaric, pentadecanoic, tridecanoic, undecanoic, pelargonic, nonadecanoic, arachidic, lignoceric, oleic, erucic, palmitoleic, linoleic, linolenic, and dehydrated castor oil acids, and tall oil fatty acids.

The proportion of fatty acid to ferric oxide determined as muffle furnace ash in the starting pigment can range from 0.2 parts to 1.2 parts by weight of acid for each part of ferric oxide ( $\text{Fe}_2\text{O}_3$ ), preferably using the lower molecular weight acids at the lower end of the range, the higher molecular weight acids at the higher end of the range; intermediate acids, such as lauric acid, are satisfactory over the entire range. The preferred range is 0.3 to 0.8 parts of 8-16 carbon atom fatty acids per part of ferric oxide. The use of the proportions set out ordinarily results in 30% to 99% of the fatty acid being bound by salt linkages to the pigment particles.

It has been established that, because of steric hindrance of the fatty acid molecules containing at least 8 carbon atoms, only about 40% of the surface area of the pigment particle can be molecularly coated with fatty acid bound by salt linkages. Analytical measurement of the free fatty acid content and the content of surface-bound fatty acid in reference to the content of  $\text{Fe}_2\text{O}_3$  provides a means for determining the approximate surface area and size of the ferric oxide core of the pigment particles.

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- In carrying out the initial step of treating the water - wet pigment pulp with the hydrophobic acid, any water - immiscible volatile organic liquid, preferably one boiling in the range 80°C.—200°C., can be used as the diluent for the hydrophobic acid provided it is a solvent for the acid, non - reactive under the treating conditions, and adequate as a compatible diluent in the liquid coating composition in which the pigment product is to be incorporated; such liquids are usually capable of functioning as a means for removing water in the vapour phase, and this is very desirable. Hydrocarbons such as toluene, xylene, high solvency petroleum naphthas and mineral spirits as preferred diluents. Xylene and toluene are particularly preferred diluents because they are most adaptable for use in a wide variety of organic coating compositions.
- The amount of the volatile organic diluent used in treating the pigment with the hydrophobic acid is not critical, and can be varied to provide a slurry of suitable consistency for agitation during the treatment. Ordinarily 25% to 75% by weight of the organic diluent based on the total weight of the fatty acid, iron oxide and organic diluent is a practical range, 30% to 50% being preferred. The use of less than 25% of the diluent necessitates a longer processing time to reach equilibrium, and the use of more than 75% offers no advantages and may require removal of diluent at a later stage to provide a practical concentration of pigment in the finished product.
- The treatment of the water-wet pigment with the fatty acid is preferably carried out at a temperature in the range of about 50°C. to about 70°C. While lower temperatures with a longer treating period can be used, it is desirable to avoid temperatures which cause precipitation of the fatty acid from solution. Higher temperatures, up to the boiling point of the volatile constituents, can be used, but it is preferred to operate at a lower temperature so as to permit removal of a major proportion of the free water by decantation and then to raise the temperature to remove the remaining free water by azeotropic distillation, with the aid of the organic diluent.
- The preferred treating period is about 60 minutes with moderate agitation, but it can be as short as about 30 minutes when the slurry contains a high concentration of the diluent, or even as short as 15 minutes if in addition the agitation is relatively vigorous. Ordinarily there is no advantage in extending the period beyond one hour unless the slurry is dense and agitation is mild. There are no adverse effects when the treating period is extended e.g. to 8 hours.
- After the initial treating period, agitation and heating are stopped to permit water to separate. Ordinarily this settling stage requires 30 to 60 minutes, though a major proportion of the water will usually separate out in 15 minutes. The separated water is best removed by decantation. The length of the settling period is not critical, inasmuch as any free water not removed by decantation is subsequently removed by distillation. The separated water can if desired be removed centrifugally using centrifugal forces of low magnitude, instead of by decantation.
- After the removal of the water in this way, moderate agitation of the residual composition is resumed, and its temperature is raised to initiate the removal by distillation of the remaining free water. Distillation is continued until no further separation of water in the distillate is observed, or until the temperature of the composition is about equal to the boiling point of the organic solvent when, as is usual, this is higher than 100°C.
- The resulting liquid dispersion of hydrophobic hydrous ferric oxide pigment in the volatile organic diluent is then subjected to fractionation by centrifugal means to remove, as a pigment sludge, all pigment particles of a size capable of scattering visible light. The centrifugal fractionation is usually most conveniently carried out, and the best separation effected, when the composition contains at least 50% and preferably 50—75% by weight of the organic diluent, and any further diluent needed to bring the amount present to such a level may be added. The fractionation can, however, be conducted at still lower concentrations of pigment, the desired practical concentration of pigment in the final product dictating the starting concentration.
- Fractionation is preferably carried out at centrifugal forces corresponding to the range 9000 g. to 16,000 g., which are representative of centrifugal forces obtained in commercially operated centrifuges and super-centrifuges. Separators which develop a centrifugal force of 6000 g. to 9000 g. can be used, but at this level the rate of separation is slower than is ordinarily desired in commercial operations. Still lower levels of centrifugal force can be used to effect fractionation, though a centrifugal force significantly below 600 g. is practical only for experimental purposes. Ultra-centrifuges which develop centrifugal forces up to 70,000 g. can be used to effect the fractionation more rapidly, but such devices are available only in laboratory sizes which are inadequate for commercial production.
- The fractionation time required to effect the substantially complete removal as a pigment sludge of particles capable of scattering visible light varies with the particular dimensions of the centrifuge and the magnitude of the forces developed therein. The lower limit of particle size for light scattering is about 30 millimicrons, but as the precise measurement of particle sizes of this order is difficult, an empirical test is used to determine whether a given fractionation is adequate. Thus in the practice of this invention, adequate fractiona-

tion is that which provides a product which when subjected to further fractionation for 15 minutes with 100,000 r.p.m. ultra - centrifuge having an effective rotor diameter of 1 inch, such as is used in blood analysis, causes separation of not more than 3% by volume of solids, based on the total volume of solids. Such a product is denoted by the expression "substantially free from pigment particles capable of scattering visible light" as used in this specification. Fractionation which provides at least this quality of product is accomplished in a fractionation time ranging from about 30 minutes using a centrifuge in which a force of 6000 g. is developed to about 2 minutes at a centrifugal force of about 70,000 g. For ordinary commercial centrifuges and super - centrifuges in which forces of 9000 g. to 16,000 g. are developed, a suitable fractionation time will be between about 18 minutes and 6 minutes respectively. In continuous operations the desired fractionation time is controlled by the rate of feed to the centrifuge. Feed rates ranging from about 10 gallons per hour at 9000 g. to about 75 gallons per hour at 16,000 g. are practical in commercial operations. With laboratory model Sharples Model 1A Ultra - centrifuge, a feed rate ranging from about .3 gallons per hour at 9000 g. to about 2 gallons per hour at 60,000 g. was satisfactory.

The improved hydrophobic hydrous ferric oxide pigment product obtained in accordance with the invention is readily dispersed by simple mixing in liquid compositions comprising a hydrophobic organic film-forming material and a volatile organic liquid which is a diluent and/or solvent therefor. The high shearing forces and large amounts of mechanical energy ordinarily associated with the dispersing of pigments are not required. Especially when the pigment composition contains an aromatic hydrocarbon solvent as the diluent it is preferred that the volatile organic solvent or diluent for the film-forming material should contain a preponderance of volatile hydrocarbon when the pigment and the film-forming material are initially mixed. After the pigment has become uniformly mixed into the film-forming composition, other volatile organic diluents and/or solvents may be added, such as esters, ketones, alcohols, and petroleum naphthas, as may be necessary to obtain the desired solvent balance for the particular film-forming material used. The choice of such volatile organic solvents and diluents is not critical, and any of the volatile organic solvents and mixtures of solvents and diluents ordinarily used in the formulation of organic coating compositions which deposit a film-forming material as a clear transparent film on evaporation of the organic liquid can be used. It is desirable that the solvents and diluents be dry, that is sufficiently free from water for the final liquid coating composition

to contain less than 1.2%, preferably less than .7%, of free water.

Organic polymers suitable as the hydrophobic film-forming material include for example: cellulose nitrate, cellulose acetate, cellulose propionate, cellulose acetobutyrate, ethyl cellulose, polyester resins, short oil length alkyd resins, urea/formaldehyde resins, melamine/formaldehyde resins, polyether resins such as those derived from bis - phenol and epichlorohydrin, vinyl acetate homopolymer and copolymers, vinyl propionate homopolymer and copolymers, vinyl chloride homopolymers and copolymers, vinyl acetal polymers, methyl methacrylate polymers, butyl methacrylate polymers, ethyl acrylate polymers, acrylonitrile/acrylic ester copolymers, acrylonitrile/methacrylate ester copolymers, styrene/acrylic ester copolymers, 1,3 - butadiene homopolymer, 1,3 - butadiene/acrylonitrile copolymers, 1,3 - butadiene/styrene copolymers, polymeric dihydric alcohol diesters of methacrylic acid, oleoresinous varnishes, and glyceride drying and semi - drying oils. (Short oil length alkyd resins contain chemically bound fatty acid in amount up to 40%, by weight, usually 25-40%, by weight, calculated as the fatty acid triglyceride). These organic film-forming materials can be in admixture with compatible modifiers, such for example as plasticizers. The composition can also include other adjuvants at the conventional concentrations, such as metallic driers, silicone fluid, fungicide, thixotropy agents, and ultra-violet screening agents.

The compositions can contain other transparent pigments and light-stable organic colouring matter to modify the colour produced by the iron oxide pigment. Because the significant characteristic of the pigments of the invention is the increased brilliance and transparency which they impart, the use of significant proportions of opaque pigments, which mask their advantage, will ordinarily be avoided. The presence of reflective aluminium flake pigment or bronze flake pigment in the composition to provide metallic finishes enhances the brilliance and increases the two-tone effect. The proportion of metallic flake can be varied widely, but preferably it should not be at a level at which the metallic opacity is significant and the transparency of the iron oxide pigment is reduced.

The coating compositions can vary widely in non-volatile content. It is practicable to apply the coating compositions at a non-volatile content as low as 5%, and some coatings can be applied at a non-volatile content as high as about 60% by weight. The ordinary range of non-volatile content is about 15% to 45% by weight. The proportion of pigment composition to total organic film-forming material is preferably between about 10 and 40 parts of the pigment for each 100 parts by weight of organic film-forming material. While

as little as 5 parts of pigment can be used, the colour contribution at this level is very small. Compositions can contain as much as 50 parts of the pigment on the indicated basis, but at this level the compositions are susceptible to gelation during storage.

The following Examples illustrate the invention. All parts are on a weight basis unless otherwise indicated.

#### EXAMPLE I

##### A. Preparation of Hydrous Ferric Oxide Pigment

278 Parts of ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) were dissolved in 1000 parts of water, and to this solution were added 18.6 parts of sodium chlorate ( $\text{NaClO}_3$ ) and commercial concentrated sulphuric acid in amount sufficient to provide 49 parts of  $\text{H}_2\text{SO}_4$ . The solution was heated to about  $82^\circ\text{C}$ . and held at this temperature for about 30 minutes to oxidize the ferrous iron to ferric iron. A solution of 117 parts of caustic soda in about 500 parts of water was slowly added to resulting solution of ferric sulphate over a period of about 20 minutes to precipitate the ferric iron as a hydrous ferric oxide. After addition of the caustic, the aqueous slurry had a pH of about 4.0. (Ordinarily the pH will be in the range of 3 to 5 and the amount of caustic may be so chosen as to give the preferred pH of 4.0.) After striking the pigment, the aqueous slurry was maintained at a temperature in the range of  $82^\circ\text{C}$ . to  $88^\circ\text{C}$ . and stirred with moderate agitation for about 2 hours. Thereafter the precipitated hydrous ferric oxide pigment was separated from the mother liquor and washed with water until the filtrate was free from water-extractable sulphates and chlorides.

##### B. Treatment of the Water - Wet Hydrous Ferric Oxide Pigment with the Monocarboxylic acid.

159 Parts of commercial lauric acid (refined coconut oil fatty acids containing about 95% lauric acid) were dissolved in 378 parts of industrial xylene [B.R. (Boiling Range)  $135^\circ\text{C}$ . to  $146^\circ\text{C}$ ., A.P. (Aniline Point)  $-44^\circ\text{C}$ .] in a vessel equipped with means for agitation, heating, decantation and distillation. The mixture was heated to about  $50^\circ\text{C}$ . and moderately agitated to facilitate dissolution of the fatty acids. To the resulting solution was added an amount of the above described water - wet hydrous ferric oxide pigment corresponding to 463 parts of dry weight of pigment. Moderate agitation and heating of the mixture at a temperature in the range of  $50^\circ\text{C}$ . to  $60^\circ\text{C}$ . was continued for about one hour. Then agitation and heating were stopped, and the mixture was allowed to separate into a non-aqueous and an aqueous phase during a 30 minute settling period. The aqueous phase was removed by decantation. After this initial removal of water, the residual composition in the transfer kettle was heated to about  $92^\circ\text{C}$ . and the remaining water was

removed by azeotropic distillation. Distillation was stopped when the vapour temperature reached  $135^\circ\text{C}$ . The residual liquid hydrophobic pigment product, free from unbound water, consisted essentially of ferric oxide pigment surface-coated with lauric acid bound by salt linkages, a small proportion of uncombined fatty acids, and industrial xylene as the volatile organic diluent.

##### C. Pigment Fractionation

The liquid pigment composition resulting from the described process Step B, had a non-volatile content of about 60% by weight. It was now diluted with industrial xylene in the proportion of 1 part of xylene by weight for each two parts of the composition to provide a diluted product with a non-volatile content of about 40% by weight. This diluted product was then subjected to fractionation by centrifugal means in which high centrifugal forces were developed.

A Model 1A Sharples Ultra - centrifuge operated at 50,000 r.p.m. provided a centrifugal force of about 62,000 g. Operated at lower speeds, centrifugal forces were developed which were comparable to those found in commercial production centrifuge units, such as 16,000 g. for a super - centrifuge and 9500 g. for Sharples D-2 series. This latter force was developed in the Model 1A at 19,500 r.p.m.

The desired pigment fractionation times corresponding to the indicated centrifugal forces were:

Force	Fractionation Time
62,000 g.	140 seconds
16,000 g.	540 seconds
9,500 g.	910 seconds

In a typical fractionation at 16,000 g. a lot of the liquid hydrophobic pigment dispersion from Step B at 40.53% non-volatile content was fed into the centrifuge at about 26 ml. per minute and the liquid product, pigment sludge and rework was recovered. A second lot was similarly fractionated starting with a non-volatile content of 46.1% fed at a rate of 35 ml. per minute and recovering the liquid product, pigment sludge and rework. A third lot was similarly fractionated, starting with a non-volatile content of 37.7% fed at a rate of 35 ml. per minute and recovering the liquid product, pigment sludge and rework. The entire amount of rework was combined and fractionated as lot 4. In continuous commercial operation of the centrifugal separation no rework is involved, in contrast to batch operations. The respective lots of pigment product and pigment sludge were separately analyzed for non-volatile content,  $\text{Fe}_2\text{O}_3$  content as muffle furnace ash, water content and fatty acid content. There was no significant analytical difference between the respective lots of the product. The respective lots of pigment sludge were similarly found to be analytically

- equivalent. The weight ratio of fatty acid to  $\text{Fe}_2\text{O}_3$  in the feed composition was .612, the average ratio in the product was .813 and the average ratio in the recovered sludge was .308.
- 5 Of the respective proportions of fatty acid present in the feed, product and pigment sludge, less than 5% was extractable as free fatty acid, indicating that in each case at least 95% was bound by salt linkages.
- 10 Using the proportion of fatty acid chemi-

cally bound to the surface area of one gram of iron oxide pigment particles and the recognized dimensions of  $51.1\text{\AA}^2$  ( $\text{\AA}$ =Angstrom) cross-sectional area and  $18.45\text{\AA}$  length for a single molecule of lauric acid, the specific surface of the  $\text{Fe}_2\text{O}_3$  particles expressed in square metres per gram can be determined approximately. The particle diameter of the  $\text{Fe}_2\text{O}_3$  core of the pigment can be determined approximately therefrom using the equation

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$$\text{Particle Diameter} = \frac{5.24 (\text{Specific Surface } \text{Fe}_2\text{O}_3)}{6}$$

- cited in E. K. Fischer's "Colloidal Dispersions" John Wiley and Sons, Inc. (1950), 5.24 being the density of  $\text{Fe}_2\text{O}_3$ . The average pigment particle  $\text{Fe}_2\text{O}_3$  core diameter found in this way was ordinarily of the order of magnitude of about 1—10 millimicrons. The average particle diameter of the hydrophobic pigment particles corresponds to the average  $\text{Fe}_2\text{O}_3$  core diameter plus  $36.9\text{\AA}$ , representing the length of two molecules of lauric acid.

- The ratio of bound acid to  $\text{Fe}_2\text{O}_3$  in the centrifugally fractionated pigment product was greater than the ratio in the feed composition, indicating a greater surface area and correspondingly a smaller average particle size than in the feed. The pigment sludge removed by centrifugal fractionation contained a significantly lower ratio of bound acid per unit weight of  $\text{Fe}_2\text{O}_3$ , indicating the the pigment particles in the sludge are significantly larger and their surface area per unit weight is smaller than in the improved product. The water content of the pigment sludge was significantly greater than that of the product, further indicating that the pigment particles in the sludge are of larger diameter and contain relatively more bound water which is not exposed at the surface of the pigment particle.

#### EXAMPLE II

- An improved hydrophobic ferric oxide pigment product was prepared in the same manner as described in Example I with the exception that in the transfer Step B a greater proportion of the lauric acid was used. 218 parts of the refined coconut oil fatty acids used in Example I were dissolved in 400 parts by weight of industrial xylene the solution was heated to about  $60^\circ\text{C}$ . and an amount of water - wet hydrous ferric oxide corresponding to 382 parts of dry weight pigment was slowly added to the solution of fatty acid. After the mixture had been agitated for one hour at a temperature in the range of  $50^\circ\text{C}$ . to  $60^\circ\text{C}$ . agitation and heating were stopped and the mixture was allowed to settle for 15 minutes. The separated aqueous layer was removed by decantation and the residual material was heated with agitation to about

$92^\circ\text{C}$ . and azeotropic distillation was initiated to remove the remaining water. Distillation was stopped when the vapour temperature reached  $135^\circ\text{C}$ .

The residue was diluted to about 40% non-volatile content with xylene and then fractionated centrifugally as described in Step C of Example I to give a clear liquid product free from pigment particles which scatter visible light and a pigment sludge containing pigment particles which scatter visible light. Except for the content of uncombined fatty acid, this improved pigment product was equivalent to the product of Example I. Analysis of the product and the sludge for bound and free fatty acid indicated that the salt-linked fatty acid contents were the same as those of the product and sludge in Example I, and that the free acid represented the excess corresponding approximately to the difference in total fatty acid between Examples I and II.

#### EXAMPLE III

Another improved pigment product was prepared following the procedure described in Example I, with the exception that tall oil fatty acids were substituted on a molecular basis for the commercial lauric acid in Step B. Since the average molecular weight of tall oil fatty acids is 280, in comparison with 200 for lauric acid, 195 parts of tall oil fatty acid were dissolved in 400 parts of industrial xylene for the treatment of an amount of water-wet pigment corresponding to 405 parts of dry weight pigment. After water removal by decantation and azeotropic distillation, and centrifugal fractionation as described in Step C to remove the pigment sludge containing pigment particles which scatter visible light, the resulting improved pigment product was equivalent to the product of Example I. Analytically on a weight basis, this product had a fatty acid content intermediate between that of Example I and that of Example II.

#### COATING COMPOSITIONS.

In the preparation of coating compositions, the improved pigment products of the foregoing examples were simply mixed with hydrophobic organic film-forming materials in the

presence of suitable organic diluents and/or solvents for the film-forming material. The following examples are representative coating compositions which are adequately durable for use as automobile finishes or as tinting enamels to be used in combination with metallic tinting enamels or ordinary pigment tinting enamels in the preparation of such finishes.

## EXAMPLE IV

## Lacquer Enamel

First Portion	Parts by Weight
High Solvency Petroleum Naphtha (B.R. 95°—142° C. A.P. 16° C.)	7.3
High Solvency Petroleum Naphtha (B.R. 130°—195° C. A.P. —13° C.)	2.0
Blown Castor Oil	4.8
Cellulose Nitrate-Isopropyl Alcohol Wet- 70% non-volatile content	20.0
Methyl Isobutyl Carbinol	4.5
Second Portion	
Pigment Product of Example I.—40% non-volatile content in xylene	8.0
Third Portion	
Butyl Acetate	5.8
Methyl Amyl Acetate	6.8
Methyl Isobutyl Ketone	4.0
Fourth Portion	
Methyl Isobutyl Ketone	9.4
Methyl Ethyl Ketone	10.1
Dibutyl Phthalate	2.5
Coconut Oil Modified Alkyd Resin Solution 70% non-volatile content in toluene	8.0
Silicone Solution 0.25% in toluene	1.0
Isopropyl Alcohol-anhydrous	5.8
	100.0

10 The cellulose nitrate was the ordinary lacquer grade having a viscosity of about 4 seconds in Formula B ASTM Designation D-301-33.

15 The alkyd resin was a 53% oil length coconut oil modified glyceryl phthalate resin having an acid number of about 2 and a hydroxyl content corresponding to 3.2% of glycerine.

The silicone solution used as a surface active

agent to provide desirable surface effects was General Electric's Silicone Fluid SF-3.

The ingredients of the first portion were added in the order indicated and mixed for 30 minutes to form a slurry of the cellulose nitrate in the diluent mixture, which does not dissolve the cellulose nitrate. The second portion was added to the slurried first portion and mixed for about three hours. Then the in-

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5 ingredients of the third portion were added and the combined portions were mixed for about two hours, the solvency of the solvent/diluent mixture of organic liquids now being sufficient to solubilize the cellulose nitrate. Then the ingredients of the fourth portion were added and the combined portions were mixed until the product was uniform. A coating of this product on evaporation of solvent deposited a clear, transparent, brown film. While this film represents a durable coating which resists weathering ordinarily encountered by an automobile finish, the composition of Example IV preferably is used as a tinting enamel in the preparation of brilliant, glamorous metallic finishes, admixing with the tinting enamel an appropriate amount of aluminium flake or paste predispersed in a film-forming composition essentially the same as that of the improved ferric oxide tinting enamel. Ordinarily the aluminium tinting enamel contains about 5% by weight of aluminium and this tinting enamel was combined with the product of Example IV in the proportions of 0.5 part to about 20 parts of the aluminium tinting enamel and 99.5 to 80 parts of the product of Example IV.

30 Metallic enamels prepared in this manner exhibited a significantly greater degree of two-tone effect than the corresponding metallic enamels prepared from the starting hydrous ferric oxide pigment which had not been improved by the fatty acid treatment and centrifugal fractionation as described above.

35 A tinting enamel equivalent to that of Example IV was obtained when 9.2 parts of the pigment product of Example II was substituted for the 8 parts of the product of Example I in the preparation of the product of Example IV, deducting the difference from the high solvency petroleum naphtha.

40 Still another equivalent tinting enamel was produced when the pigment product of Example III was substituted for the pigment product of Example I on the basis of  $\text{Fe}_2\text{O}_3$  content in the preparation of the lacquer product of Example IV.

45 While the designation "sludge" ordinarily suggests discard material, the pigment sludge derived as the residue in the centrifugal fractionation of the fatty acid treated intermediate product has value as a pigment material. The sludge substituted for the improved pigment product of Example I in the preparation of the coating composition of Example IV at an equivalent content of  $\text{Fe}_2\text{O}_3$  and also at a content of 3.5%  $\text{Fe}_2\text{O}_3$  produced useful compositions. These products did not exhibit the superior transparency, brilliance, and two-tone effect which resulted from the use of the improved pigment, but these sludge-containing products were not significantly inferior in appearance when compared with the control enamels formulated at the same pigment levels with pigment corresponding to the starting hydrous ferric oxide pigment from which the pigment sludge and the improved pigment product were derived.

#### EXAMPLE V

##### Alkyd Resin Enamel

First Portion	Parts by Weight
Pigment Product of Example I — 40% non-volatile content	29.5
Calcium Naphthenate Solution — in mineral spirits (4% calcium equivalent)	1.5
Xylene	12.9
Second Portion	
Soya Oil Modified Alkyl Resin — 55% non-volatile in hydrocarbon solvent	56.1
	100.0

70 The alkyd resin was 46% oil length soya oil modified glyceryl phthalate resin and had an acid number of about 25 and a hydroxyl content corresponding to 0.9% of glycerine. The solvent consisted of a mixture consisting of 85% by weight of high solvency naphtha characterised by a boiling range of

130°C. to 195°C. and an aniline point of -13°C. and 15% of mineral spirits.

80 The ingredients of the first portion were mixed 30 minutes and then the second portion was slowly added thereto with agitation and mixed until uniform.



## EXAMPLE VI

First Portion	Acrylic Resin Enamel	Parts by Weight
Pigment Product of Example I — 40% non-volatile content		10.9
Toluene		14.0
Acrylic Resin Solution — 40% non-volatile content		12.4
Second Portion		
Acrylic Resin Solution — 40% non-volatile content		29.3
"Santiciser" 160-Benzyl Butyl Phthalate		6.4
Dispersion of "Bentone" 34-Organophilic Montmorillonite Clay — 30.2% non-volatile content		27.0
		100.0

("Santiciser" and "Bentone" are Registered Trade Marks)

- 5 The acrylic resin solution comprised a copolymer of 98 parts methyl methacrylate and 2 parts methacrylic acid at 40% copolymer content in a mixture consisting of 40% acetone and 60% toluene by weight. This copolymer had an average molecular weight of about 80,000 and the viscosity of the indicated solution was about 45 poises.
- 10 The dispersion of "Bentone" 34 consisted of 7% of this organophilic treated montmorillonite clay dispersed in the presence of 23.2%
- of methyl methacrylate homopolymer in solution in a solvent mixture consisting of 60% xylene, 25% toluene and 15% acetone by weight. This homopolymer had an average molecular weight of about 80,000.
- 15 The ingredients of the first portion were mixed together with agitation for five hours at 50°C. Then the ingredients of the second portion were slowly added to the first portion and the whole mixed until uniform.
- 20

## EXAMPLE VII

First Portion	Alkyd Resin Enamel	Parts by Weight
Pigment Product of Example I — 40% non-volatile content		13.8
Xylene		30.4
Second Portion		
Coconut Oil Modified Alkyd Resin Solution — 67% non-volatile content		30.8
Third Portion		
Melamine/Formaldehyde Resin Solution — 55.5% non-volatile in butyl alcohol		20.0
Fourth Portion		
Melamine/Formaldehyde Resin Solution 55.5% non-volatile content in butyl alcohol		5.0
		100.0

- The alkyd resin was a 37% oil length coconut oil modified glyceryl phthalate resin having an acid number of about 10 and a hydroxyl number corresponding to 5.6% of glycerine. This resin was 67% non-volatile content in a mixture of 50% by weight of toluene and 50% high solvency naphtha having a boiling range of 150°C. to 190°C. and an aniline point of -28°C.
- The melamine/formaldehyde resin was equivalent to American Cyanamid's "Melmec" 248-8 except for the composition of the volatile diluent.
- The first portion was mixed about 20 minutes and the second portion was slowly added thereto and mixed for one hour. Then the third portion was added and mixed for one hour and finally the fourth portion was added and the entire composition was mixed for one hour.
- These several coating compositions, evaluated in comparison with corresponding controls formulated with either the parent hydrous ferric oxide pigment transferred by ordinary means to the hydrophobic organic vehicle without centrifugal fractionation or with commercially available flushed hydrous iron oxide pigment bases, were found to be consistently and significantly better than the controls in respect of brilliance, clarity, and depth of colour with and without the presence of metal flake pigment and to exhibit greater two-tone effect when formulated as a metallic finish. The finishes derived from these compositions on loss of volatile solvent with drying or curing under ordinary conditions were found to be durable on exposure to the weather and exhibited physical properties at least equal to those of the control finishes. The improved pigment of this invention produced desirable improvements in the appearance of the finishes without alteration in serviceability and durability.
- WHAT WE CLAIM IS:—**
1. A hydrophobic iron oxide pigment composition which comprises a dispersion in a water - immiscible volatile organic liquid diluent of pigment particles comprising iron oxide which are not capable of scattering visible light and have a molecularly thin surface coating of at least one hydrophobic aliphatic monocarboxylic acid which is soluble in the organic diluent, the said acid being bound by salt linkages to the pigment particles, and the said dispersion being substantially free from pigment particles capable of scattering visible light.
  2. Hydrophobic iron oxide pigment compositions according to claim 1 comprising a dispersion in the organic diluent of ferric oxide pigment particles.
  3. Pigment compositions according to claim 1 in which the proportion of hydrophobic monocarboxylic acid is 0.2 to 1.2 parts by weight for each part by weight of pigment, and 30% to 99% of the acid is bound to the surfaces of the pigment particles by salt linkages.
  4. Pigment compositions according to any of claims 1 to 3 in which the hydrophobic monocarboxylic acids are aliphatic saturated or ethylenically unsaturated monocarboxylic acids having 6 to 24 carbon atoms in the molecule.
  5. Pigment compositions according to claim 4 in which the hydrophobic monocarboxylic acids have 8 to 16 carbon atoms in the molecule and are present in a proportion of 0.3 to 0.8 parts by weight per part by weight of pigment.
  6. Pigment compositions according to any of the preceding claims in which the hydrophobic monocarboxylic acids comprise lauric acid or a mixture of coconut oil fatty acids, or tall oil fatty acids.
  7. Pigment compositions according to any of the preceding claims in which the water-immiscible volatile organic diluent is toluene or xylene.
  8. Pigment compositions according to any of the preceding claims in which the amount of the water - immiscible volatile organic diluent is 25% to 75% of the total weight of the composition.
  9. A process for the production of hydrophobic iron oxide pigment compositions from a water - wet hydrous iron oxide pigment pulp which has an average particle size less than 100 millimicrons and a particle size distribution ranging from 1 millimicron to 300 millimicrons which comprises (a) treating the wet pigment pulp with a solution of at least one hydrophobic aliphatic monocarboxylic acid in a non-reactive volatile water-immiscible organic liquid diluent in the proportion of 0.2—1.2 parts by weight of acid for each part by weight of iron oxide whereby the pigment particles are provided with a molecularly thin hydrophobic surface formed by the bonding of the said acid salt linkages to the surface of the pigment particles, (b) removing free water from the resulting composition, and (c) fractionating the resulting composition centrifugally, if desired after adjusting its concentration, using a centrifugal force of at least 6000 g. to separate from the composition a pigment sludge fraction leaving a composition substantially free from pigment particles capable of scattering visible light.
  10. A process according to claim 9 in which the pigment pulp starting material has an average particle size between 10 and 30 millimicrons.
  11. A process according to claim 9 or 10 in which the pigment pulp starting material is treated with the hydrophobic aliphatic carboxylic acid in the presence of a water - immiscible volatile organic diluent which boils in the range 80° to 200°C.
  12. A process according to claim 11 in

- which the diluent is toluene or xylene.
13. A process according to any of claims 9 to 12 in which the pigment pulp starting material is treated with the hydrophobic aliphatic carboxylic acid at a temperature of 50° to 70° C.
14. A process according to any of claims 9 to 13 in which the substantially water-free pigment composition resulting from operation (b) is centrifuged at 9000 g. to 16,000 g.
15. A process according to any of claims 9 to 14 in which the substantially water-free pigment composition resulting from operation (b) contains when centrifuged at least 50% by weight of the water-immiscible volatile organic diluent.
16. A process for the preparation of a hydrophobic iron oxide pigment composition carried out substantially in accordance with any one of Examples I to III.
17. A process for the preparation of a hydrophobic iron oxide pigment composition substantially as described.
18. A hydrophobic iron oxide pigment composition prepared by the process claimed in any of claims 9 to 17.
19. A coating composition which comprises a hydrophobic organic film-forming material, a pigment composition claimed in any of claims 1 to 8 and 18, and a solvent for the film-forming material.
20. A coating composition according to claim 19, in which the proportion of the pigment composition is 10—40% based on the weight of the organic film-forming material.
21. A coating composition according to claim 19 or 20 which also comprises an aluminium flake pigment.
22. A coating composition according to any of claims 19 to 21 in which the organic film-forming material is plasticised cellulose nitrate.
23. A coating composition according to any of claims 19 to 21 in which the organic film-forming material is a mixture comprising a short oil length alkyd resin and a melamine-formaldehyde resin.
24. A coating composition according to any of claims 19—23 in which the non-volatile constituents amount to 5% to 60% by weight of the composition.
25. A coating composition according to claim 19 prepared in accordance with any one of Examples IV to VII.
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